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Dye-Sensitized Solar Cells Using Surface-Stabilized Nanocrystalline-TiO₂ Electrodes Coated by Epoxy Polymer

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Abstracts

In order to improve the thermal durability of dye-sensitized solar cells (DSCs), epoxy polymer was coated on dyed-TiO₂ electrode to prevent dye desorption under heating condition over 80°C. The covering effect on epoxy polymer was confirmed using impedance spectroscopy. Using the epoxy polymer coating with Z907 Ru dye and ionic liquid electrolyte, the DSC photovoltaic durability was improved up to 90°C, which is the highest temperature published for the DSC durability test. Although the epoxy polymer suppressed the DSC photovoltaic effect, it enhance the thermal durability; DSC coated epoxy polymer on the dyed-TiO₂ electrode was able to prolong the efficiency over 90% of the initial value at 90°C for 550 hours.

Key words: Dye-sensitized solar cells; Epoxy polymer; Ionic liquid electrolyte; Thermal durability; Heat test

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INTRODUCTION

The energy shortage and environmental pollution have been big problems for human beings in the near future. Establishment of new electric power generation system is necessary. One of the promising candidates to solve the problems is solar photovoltaic systems. In these days, therefore, a variety of solar cells have been researched and developed. The targeted price Japanese Yen (¥) per output power (W) by the photovoltaic generation until 2030 is 50 ¥/W as the Japanese government policy. This target cost is less than half of the present value.

Since expensive materials (Si, In, etc.) and/or high vacuum process have been utilized for the manufacturing conventional solar cells, the numerical target cannot be achieved. Therefore, it is necessary to develop cost-effective and efficient solar cells.

Dye-sensitized solar cells (DSC) have been considered one of the candidates of next generation solar cells. Originally, dye-sensitization effect has been found by James Moser at 1887^[1]. Afterwards, Grätzel et al. have developed the sensitization effect to the structure of solar cells, which has the possibility that the cost of manufacturing can be greatly reduced^[2-4]. The research and development for the practical utilization of DSCs have widely been performed in the university, governmental research laboratories, and the companies. The DSCs, which generate electricity by adsorbed dyes on porous TiO₂ electrode, has the performance rivals to amorphous silicon solar cells. However, the dye is easy to desorb from the TiO₂ surface under high-temperature condition^[5]. Therefore, blocking the dye desorption under heat temperature is one of the important strategy for the practical utilization. For example, in order to prevent the dye desorption, dye polymerization (between Ru dyes) has been performed^[6], but for the DSCs, acetonitrile-based volatile electrolyte was used for the experiments and the stability test was performed only under room temperature. However, car and device companies are

asking DSC durability over 100 °C for the industrial application (in private communication). In this work, therefore, in order to improve the thermal durability of DSCs, trimethylolpropane triglycidyl ether and 1,6-diaminohexane were polymerized as epoxy polymer on the surface of dyed porous TiO₂ electrode (Fig. 1). The polymer was expected to block the dye desorption from TiO₂ under the heat stress. We have tried the thermal duration test of DSCs using the epoxy polymer coating on dyed TiO₂ electrode with ionic liquid electrolyte in the range of temperature from 80 °C to 110°C. Although the DCSs could not survive over 100 °C, the DSC thermal durability was improved until 90 °C.

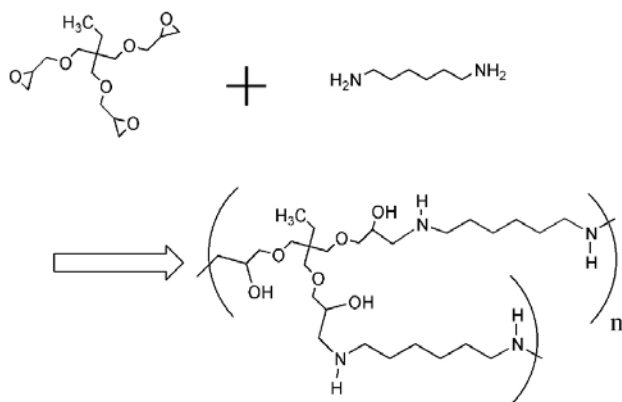


Figure 1
Reaction of Epoxy Polymer with 3-D Network

1. EXPERIMENTAL

1.1 Materials

Ethanol (Kanto Kagaku), acetone (Kanto Kagaku), acetonitrile (Wako), *tert*-butyl alcohol (Wako), H₂PtCl₆ (Tokyo Chemical Industry Co., Ltd) were used as received. H₂O was purified by distillation. TiCl₄ (Kishida Chemical Co. Ltd.) was diluted with water to 2 M at 0 °C to make a stock solution, which was kept in a freezer and freshly diluted to 40 mM with water for each TiCl₄ treatment of the FTO coated glass plates. A TiO₂ paste using 400 nm particle for light-scattering layers (PST-400C, JGC Catalysts and Chemicals Ltd.) were used as received. For transparent nanocrystalline-TiO₂ layer, 20 nm TiO₂ particles were made by using the hydrothermal crystallization method, which was converted into a screen-printing paste^[7]. The electrolyte employed was a solution of, 0.5M I₂ (99.999%, Aldrich) in a mixture of 1-methyl-3-propylimidazolium iodide (MERCK) and 1-Ethyl-3-methylimidazolium thiocyanate (MERCK) (volume ratio, 13:7)^[8,9].

FTO glass used as current collector (Solar 4 mm thickness, 10Ω/□, Nippon Sheet Glass, Japan) was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. After treatment in a UV-O₃ system (UVE-110-1H, Sen light Co. Ltd.) for 20min, the FTO glass plates were immersed into

a 40 mM aqueous TiCl₄ solution at 70 °C for 30min and washed with water and ethanol. This treatment decreased the dark current between the FTO glass and electrolyte^[10].

The layer of 20 nm TiO₂ particles for the transparent layer was coated on the FTO glass plates by screen-printing, kept in a clean box for 6min so that the paste can relax to reduce the surface irregularity and then dried for 6 min at 125 °C. This screenprinting procedure was repeated to get an appropriate thickness of 6.5~8 μm for the working electrode.

After drying of the paste layer with 20-nm TiO₂ nanoparticles the films at 125 °C, a light-scattering layer of PST-400C, containing 400 nm sized anatase particles, was deposited by screen-printing, resulting in 4~5 μm thickness. The electrodes coated with the two kinds of TiO₂ pastes were gradually heated under an airflow at 325 °C for 5min, at 375 °C for 5 min, and at 450 °C for 15min, and finally, at 500 °C for 15 min.

The TiO₂ films produced were once again treated with 40 mM TiCl₄ solution, as described above, and rinsed with water and ethanol. Then TiO₂ electrode sintered at 500 °C for 30 min by the air heating gun (BOSCH). After cooling to 70 °C, the TiO₂ electrodes were immersed into a 0.3 mM Z-907 dye solution in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio, 1:1) and kept at room temperature for 14 h to assure complete sensitizer uptake^[11].

For the epoxy polymer coating on dye-sensitized nanocrystalline-TiO₂ electrodes, trimethylolpropane triglycidyl ether (Aldrich) and 1,6- diaminohexane (Tokyo Chemical Industry Co., Ltd) were utilized as the monomers. For the 1.0 wt% polymer solution, trimethylolpropane triglycidyl ether (30mg) and 1,6-diaminohexane (30 mg) were dissolved in acetonitrile (6g). For the 2.5 wt% and 4.0 wt% polymer solutions, the amount of monomers were multiplied 2.5- and 4.0-times, respectively. The dye-adsorbed TiO₂ layers were immersed in the monomer solutions for 5 min at 50 °C, took out from the solution, and heated at 90 °C for 10 minutes on a hot plate under air for the polymerization.

To prepare the counter electrode, a hole (1-mm diameter) was drilled in the FTO glass (TEC 15 Ω/□, 2.2 mm thickness, Nippon Sheet Glass Co. Ltd., Japan) by drilling. The perforated sheet was washed with H₂O as well as with a 0.1 M HCl solution in ethanol and cleaned by ultrasound in an acetone bath for 10 min. After removing residual organic contaminants by heating in air for 15 min at 400 °C, the Pt catalyst was deposited on the FTO glass by coating with a drop of H₂PtCl₆ solution (2 mg Pt in 1 ml ethanol) with repetition of the heat treatment at 400 °C for 15 min^[7].

The dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of the ionomer Bynel 4164 (35 μm thickness, Dupont). The size of the TiO₂ electrodes used was 25 mm² (= 5 mm × 5 mm). The aperture of the

Bynel frame was 2 mm larger than that of the TiO₂ area. The hole in the counter electrode was sealed by a film of Bynel using a hot iron bar (protectively covered by a fluorine polymer film). A hole was then made in the film of Bynel by a needle. A drop of the electrolyte was put on the hole in the back of the counter electrode. It was introduced into the cell via vacuum backfilling. The cell was placed in a small vacuum chamber to remove inside air. Exposing it again to ambient pressure causes the electrolyte to be driven into the cell. Finally, the hole was sealed using a hot-melt ionomer film (Bynel) and a cover glass (0.1 mm thickness). A solder (Cerasolza, Asahi Glass) was applied on each side of the FTO electrodes.

Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 450 W xenon lamp (YSS-E40, Yamashita Denso Co. Ltd., Japan). The power of the simulated light was calibrated to 100 MW/cm² by using a reference Si photodiode equipped with an IR-cutoff filter (BS-520, Bunkou Keiki Co. Ltd., Japan) in order to reduce the mismatch between the simulated light and AM 1.5 (in the region of 350–750 nm) to less than 2%^[12]. I–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a digital source meter (6240A, ADCMT, Japan). The start voltage and end voltage of the measurement is -0.1V and 0.7V. The voltage step and delay time of photocurrent were 1 mV and 100 ms, respectively.

2. RESULTS AND DISCUSSION

Photocurrent-voltage characteristics of DSCs were measured with changing the amount of polymer: 0.0, 1.0, 2.5, and 4.0wt%. Figure 2 shows a photovoltaic characteristic related to the amount of polymer. The short-circuit current density (J_{SC} , Fig. 2a) and the fill factor (FF, Fig. 2b) were decreased with increasing the amount of polymer. Hence, the polymer coating may prevent charge transfer: $\text{dye}^* \rightarrow \text{dye}^+ + \text{electron}$ (in TiO₂). On the other hand, addition of a small amount of polymer increased the open-circuit voltage (V_{OC} , Fig. 2c). The V_{OC} increasing may be due to the suppression of charge recombination by the polymer coating on TiO₂: $\text{I}_3^- + 2 \text{electron}$ (in TiO₂) $\rightarrow 3\text{I}^-$. The resulting conversion efficiency (η) decreases with an increase of the amount of polymer (Fig. 2d), because the drop of J_{SC} was much intense than the increase of V_{OC} .

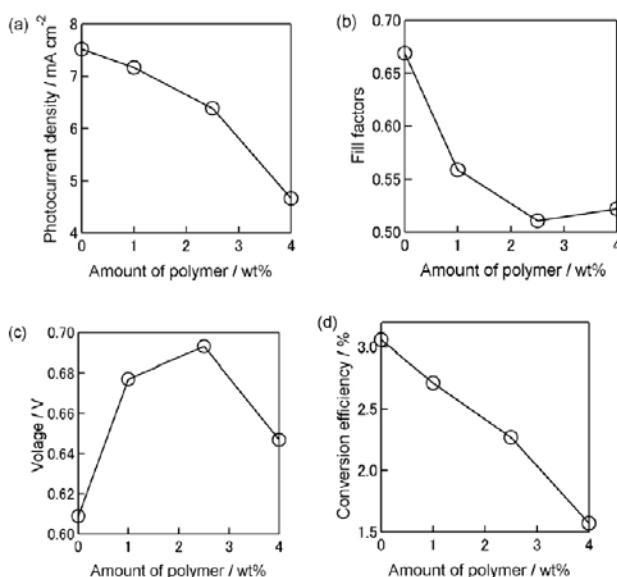


Figure 2
Variations of Photovoltaic Parameters Related with Amount of Epoxy Polymer: J_{SC} (a), V_{OC} (b), FF (c) and η (d). X-axis (Amount of Polymer) Represents the Amount of Monomer in the Solution

Figure 3a shows the electrochemical impedance spectra. The left-side, center and right-side semicircles correspond to the elements of <Pt/electrolyte>, <TiO₂/dye/electrolyte> and <electrolyte diffusion>, respectively^[13]. Each element was analyzed using a standard equivalent circuit for electrochemical cells such as DSCs^[14-16] (Fig. 3b). It is noticed that the interface resistance of <porous-TiO₂/dye/electrolyte> and the resistance of <electrolyte diffusion> increased with increase of the amount of polymer (Fig. 3c). The increase of interface resistance of <TiO₂/dye/electrolyte> with increasing the polymer may suggest the existence of epoxy polymer between dye and electrolyte. The increase of <electrolyte diffusion> resistance in the iodide electrolyte with increasing the polymer may suggest that the polymer exists in the porous-TiO₂ electrode also, and then, the diffusion of electrolyte was hindered.

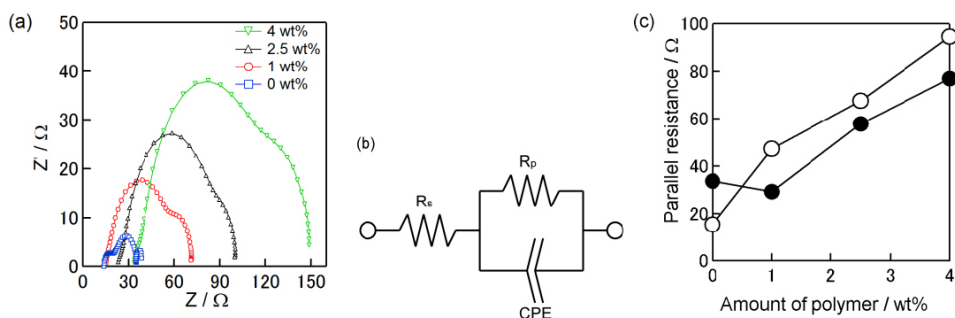


Figure 3
(a) Cole-Cole Plots of Impedance Measurements for Epoxy Polymer Coated DSCs with Ionic Liquid Electrolyte;
(b) an Equivalent Circuit to Analyze Electrochemical Cells such as DSCs (R_s : Series Resistance; R_p : Parallel Resistance; CPS: Constant Phase Element); (c) Variations of Parallel Resistances Related with Amount of Epoxy Polymer in Fig. 3(a) (Open and Close Circles Represent Fitted Results of Center and Right Semicircles, Respectively)

DSC thermal durability tests have been performed from 80 °C to 110 °C. Figure 4 shows the variations of DSC maximum output (P_{max}) in the duration of each thermal test. The DSCs were stable under 80 °C thermal test regardless of the existence of the polymer. At 90 °C thermal test, the DSC thermal durability was improved by addition of epoxy polymer. The epoxy polymer on the dyed-TiO₂ electrode was able to prolong the DSC efficiency over 90% of the initial value at 90 °C for 550 hours. On the other hand, the P_{max} of polymer-coated DSCs was decreased gradually as DSCs without polymer. At 100 °C thermal test, the durability of the polymer addition cell has worse than that without polymer. At 110 °C thermal test, it was confirmed that DSCs lost the photovoltaic function at once regardless of the presence of polymer.

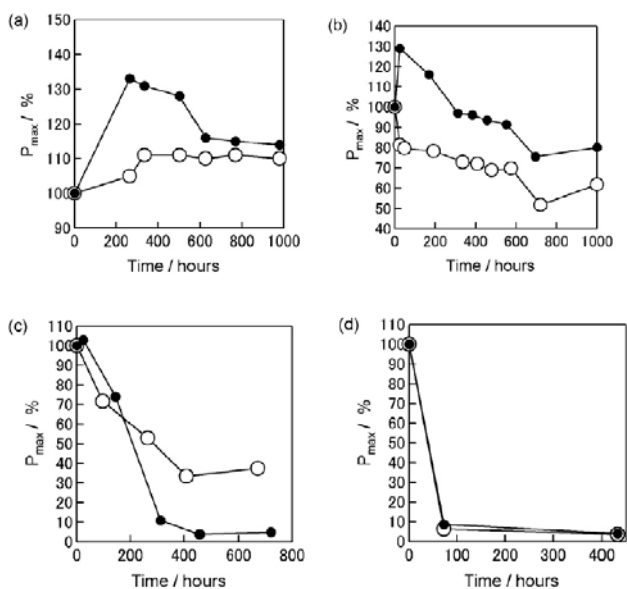


Figure 4
Thermal Durability Test of Ionic-Liquid DSCs with/without Epoxy Polymer Coatings at 80 °C (a), 90 °C (b), 100 °C (c) and 110 °C (d); Open Circles: Without Polymer; Closed Circle: with Epoxy Polymer. Each Initial P_{max} Value was Scaled to 100%

CONCLUSION

Since electron transfer between electrolyte and dyed-TiO₂ electrode was able to be reduced by epoxy polymer coating, the open-circuit voltage was increased, and the short-circuit photocurrent and the fill factors were decreased. Under the heat test at 80 °C, DSCs using ionic liquid and Z907 Ru dye showed the durability for 1000 hours regardless of epoxy polymer coating. During 90 °C heat test, the DSC durability was improved by adding polymer. However, the epoxy polymer has no effects over 100 °C. For the future progress of DSC thermal durability, it is necessary to examine the polymer performance precisely. We wish that this report contributes to the future of DSC applications.

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